Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

ON FLUCTUATIONS IN THE COMPOSITION OF NATURAL GAS.*

BY FRANCIS C. PHILLIPS.

Presented by the C. M. Warren Committee, October 12, 1898.

Received October 12, 1898.

AT the mills and factories of the Pittsburgh region the opinion is often expressed by men in charge of steam boilers where natural gas is the fuel used, that the gas fluctuates in its heating power, and that at certain times more gas must be used than at others to accomplish the same work. Changes of pressure in the mains, owing to varying demands upon the supply, requiring that the valve controlling the admission of gas to a boiler fire should occasionally be opened more widely, might readily lead to the supposition that the gas at such times possesses less heating power and consequently a different composition.

No data as regards results in practice have been obtainable, but in analyses of gas from various wells in the Pittsburgh region reasons have been found for supposing that slight fluctuations actually occur in its composition. With a view to a more complete study of the question, the experiments described in this paper were carried out.

As regards the character and number of its chief constituents natural gas differs widely from coal gas, and from gas manufactured at high temperatures in the various forms of producers. While in artificial gas unsaturated compounds are present in great variety, natural gas is composed mainly of hydrocarbons of the paraffin series, associated with very small quantities of nitrogen, carbon dioxide, and water vapor. The olefines, represented mainly by ethylene, are found sometimes in extremely minute proportion, so minute in fact that quantitative determinations are a matter of difficulty, although they are qualitatively recognizable when large volumes of gas are employed. Traces of organic sulphur compounds are also present. Free hydrogen, carbon monoxide, hydrogen sulphide, and oxygen do not occur.

---

* Acknowledgment is here made of aid received from the C. M. Warren Fund of the American Academy of Arts and Sciences, in conducting the experiments described in this paper.

It is a difficult matter to single out any of the constituents of natural gas as specially suited for a series of determinations having for their purpose to ascertain whether fluctuations actually occur in its composition. One of its constituents — nitrogen — seems to be less prone than the others to enter into chemical changes locally in the rocks, and therefore less likely to undergo diminution in the original gas as it is stored in the interstices of the sandstones and limestones of the Devonian formation. It might be proper to begin such a study with nitrogen.

Under the term nitrogen is here understood the incombustible residue obtained when natural gas is burnt in such manner as to prevent the admixture of air or oxygen with the products. That the element nitrogen is actually contained in natural gas has been frequently shown by passing the gas over heated magnesium. The magnesium, on being afterwards moistened, yielded ammonia, recognizable by its odor and reactions, and indicating the presence of nitrogen in the original gas.

The method employed for the determination of nitrogen consisted in burning a measured volume of natural gas by passing it over heated copper oxide. The resulting steam was condensed and the carbon dioxide absorbed by potassium hydroxide solution, leaving the residual nitrogen to be measured over mercury. This adaptation of the Dumas method has been proposed by Stöckmann for the determination of nitrogen in coal gas.* Arth has described an apparatus for a similar purpose, the gas measurements being made over water.†

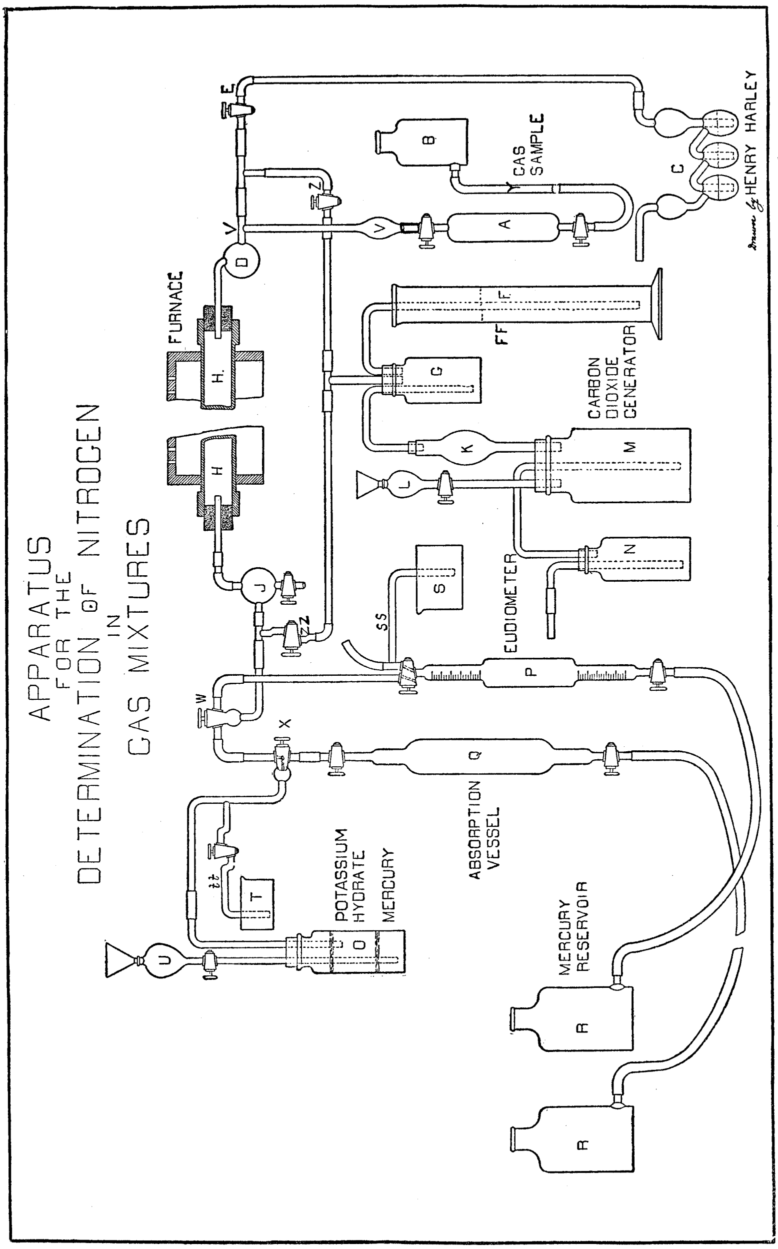
Description of the Process.

The gas sample was collected in a glass cylinder of from 150 to 400 c.c. capacity, and having stopcocks at both ends. In the drawing of the apparatus *A* represents the gas sample vessel with its stopcocks and capillary endings. Vessels of 150 c.c. proved sufficiently large for the determination, although in the later work, where it was desirable to collect a larger volume of the residual incombustible gas, vessels of 350 to 400 c.c. were used. These vessels were calibrated by weighing the mercury required to fill them. They were filled with gas under slight excess of pressure (about two ounces). With a view to determining by calculation the volume at 0° and 760 mm. pressure of the

---

* Zeitschrift für Analyt. Chemie, 1875, p. 46.

† Bull. Soc. Chim., 1897, p. 30.


APPARATUS
FOR THE
DETERMINATION OF NITROGEN
IN
GAS MIXTURES
FURNACE
H.
H
D
V
E
Z
ZZ
J
B
GAS SAMPLE
C
A
V
F
FF
G
CARBON DIOXIDE GENERATOR
K
M
L
N
EUDIOMETER
S
SS
P
W
X
Q
ABSORPTION VESSEL
POTASSIUM HYDRATE
MERCURY
T
tt
O
U
MERCURY RESERVOIR
R
R
Drawn by HENRY HARLEY

contained gas, the vessels after return to the laboratory were placed vertically in a large box having glass sides, and in such a position that the lower stopcock projected through a thick rubber disk set in the bottom of the box and having an opening just large enough for the stopcock to pass through it. The temperature in the box was indicated by a thermometer, which could at all times be read through the glass panes. When this temperature had remained constant for at least one hour, the lower stopcock was opened for an instant allowing the surplus gas to escape. A glass tube, connected by rubber joint with the lower end of the stopcock, and just touching, but not dipping under the surface of water, afforded a simple and safe means of preventing the possibility of the entrance of air during the equalizing of the pressure. After opening and shutting the stopcock the pressure of the contained gas was assumed to be that of the air outside, as indicated by the barometer. A drop of water was always introduced into the sample vessel before it was filled, so that the gas could be regarded as saturated with moisture when used for analysis.

The gas vessel was connected with a mercury bottle *B*, the capillary tubes at the ends of the cylinder having been filled with mercury before the connections were made. By raising the bottle *B* and opening the stopcocks the gas was slowly driven over from *A* through the glass tube *VVD* into the porcelain combustion tube *HH*, which contained a layer of heated copper oxide forty centimeters long. The porcelain tube was heated in a combustion furnace (partly shown in the sketch). The products of combustion of the gas passed by way of the glass bulb *J* and the stopcocks *W* and *X* to the absorpion vessel *Q*, in which the carbon dioxide was absorbed by solution of potassium hydroxide. This solution was delivered over when needed from the bottle *O*, by pouring mercury into the tap funnel *U*. The residual gas, after the absorption of the carbon dioxide in *Q* was then caused to return by the same route to the cylinder *A*, by adjusting the levels of the mercury reservoirs *B* and *R*. A third passage of the gas over from *A* to *Q* rendered it certain that all hydrocarbons were completely burnt. The bulb *J*, and the combination of bulb with three way tube *DVV* served to condense and hold as water any steam due to burning of hydrogen of the gas in the combustion tube, and prevent its return into the heated porcelain tube. These bulbs proved very necessary to prevent breakage. The stopcock on the bulb *J* served to discharge this condensed water. As it was necessary to rinse the porcelain tube and its glass connections after the passage of the gas from *A* to *Q*, or from *Q* to *A*, this was accomplished by means of a slow stream of carbon dioxide generated by the action of concentrated hydrochloric acid upon calcite in the large jar *M.* This jar contained about five pounds of calcite at starting. The escaping carbon dioxide passed through fragments of calcite in the tube *K*, and through water in the bottle *G.* From this wash-bottle the gas stream could be deflected to the right hand end of the combustion tube, as seen in the sketch, entering this tube by the stopcock *Z* in rinsing gas into the absorption vessel *Q*, or to the left, by way of the stopcock *ZZ* in rinsing gas back into the vessel *A*. In this manner the rinsing out of the products of combustion into either *A* or *Q* could be made very complete. The tube *F*, descending into water in the open cylinder *FF*, served as a safety valve to permit the escape of surplus carbon dioxide from the generator, and thus any unsafe pressure in the apparatus was avoided. The carbon dioxide could, therefore, be generated freely and utilized only in so far as it was needed. It is to be observed that the long glass tube connecting the stopcocks *Z* and *ZZ* lies in the same horizontal plane with the combustion tube *HH*, although in the sketch it appears lower, in order that the arrangement of parts may be rendered clear. The carbon dioxide having been absorbed in *Q*, the residual gas was ready for measurement which was accomplished in the eudiometer *P* over mercury. This eudiometer was of 100 c.c. capacity, being made very short as shown (about forty centimeters long). It was graduated only in its uppermost and lowermost portions. This is a convenient form of eudiometer where mercury is used, as it avoids the great pressure of a high mercury column, and consequent danger of leakage through the stopcocks, so common where a high column of mercury is used. It is easily seen that by lowering sufficiently the bottle *R* any volume of gas, up to 100 c. c. may be readily measured. The combustion furnace stood somewhat higher than the upper end of the eudiometer. It was surrounded closely by sheet iron sides, which served to carry upward the waste heat. No difficulty was experienced in maintaining a constant temperature about the eudiometer, as indicated by a thermometer reading to 0.05°, placed in contact with its sides. By reason of the strong upward draught produced by a sheet iron box placed around and in close contact with the sides and ends of an ordinary combustion furnace, much may be done towards diminishing the discomfort of the experimenter, while the temperature of the interior of the furnace is increased, and the ends of the tube are more readily kept cool. The tube *tt*, dipping into water in the beaker *T*, serves to discharge the absorption vessel after a determination. In a similar manner the eudiometer may be discharged of its contents by the tube *ss* dipping into the beaker *S*. The tube *E* serves to discharge carbon dioxide through a Liebig's bulb having a water seal, when the apparatus is being cleared of air preparatory to a determination. The various forms of stopcocks used are sufficiently indicated by the sketch. The time required for a nitrogen determination was from one and a half to two hours when 150 c. c. of gas were used. Two or three days were sometimes occupied in expelling the last traces of air from the apparatus by the slowly passing carbon dioxide stream preparatory to a series of determinations.

The potassium hydroxide solution was of 1.258 specific gravity, as recommended by Kreusler,* and the measurement of the nitrogen was always made with a little of the fresh solution resting upon the mercury in the eudiometer. The mercury reservoirs, *R*, *R*, were attached to supports sliding vertically in wooden frames (not shown), and the reservoir connected with the eudiometer could be adjusted by screw movement so as to bring the mercury in the reservoir and that in the eudiometer to the same level. Readings were made by an accurate cathetometer. The pressures of mercury columns were all calculated at 0°.

A very high temperature was found to be necessary for the complete combustion of the hydrocarbons of natural gas, under the conditions of the method, the excess of carbon dioxide produced causing retardation. No difficulty was experienced, however, as repeated tests demonstrated that the residual gas did not contain carbon monoxide or free hydrogen. Moreover, it was repeatedly found that on passage of the residual gas for a fourth and fifth time through the copper oxide, and absorption of the carbon dioxide, no further reduction of volume was produced. The constantly increasing amount of reduced copper in the porcelain tube, as combustion goes on, serves to prevent the escape undecomposed of any oxides of nitrogen, should such compounds tend to form during the process.

In order to procure pure carbon dioxide for the Dumas method of nitrogen determination in organic bodies, it has been recommended that the marble to be used be first pulverized and then boiled in water before its carbon dioxide is liberated by the action of an acid. Bernthsen † frees the pores of the marble from air by exhaustion with an air pump. In experiments tried with a view to producing pure carbon dioxide these methods have not always proved satisfactory. The carbon dioxide stored in liquid form in steel cylinders was tried. It was found, however, that the gas leaves a considerable volume of unabsorbed residue when treated with the solution of a caustic alkali. Sodium carbonate was tried instead of marble. A hot saturated solution of the salt was allowed to crystallize in the generator and the mother liquid poured off. The carbon dioxide produced by action of an acid is purer than that from marble, but the evolution of the gas is tumultuous and uncontrollable. Experiments were tried with marble from various localities, but with little success. A marble from Tate, Georgia, was found to yield very pure carbon dioxide after it had been coarsely pulverised and well boiled in water. Another sample of apparently the same rock, from the same locality, yielded after similar treatment a small residue of gas unabsorbed by potassium hydroxide solution. A calcite from Lampasas, Texas, in translucent cleavable crystals, was found to yield satisfactory results. The mineral was crushed coarsely, boiled for six hours in water, and then transferred with a portion of the boiled water to the generator. The carbon dioxide evolved proved to be very pure. Experience has shown that no reliance can be placed upon marble or calcite as a source of carbon dioxide because a specimen of apparently the same mineral known to come from the same locality has proved satisfactory. Every batch must be separately tested as regards the purity of the carbon dioxide which it evolves.

---

* Zeitschrift für Analyt. Chemie, 1885, p. 445.

† Zeitschrift für Analyt. Chemie, 1882, p. 63.

To overcome the danger of the action of strong alkali upon stopcocks in such work, it was necessary to use an unsaponifiable lubricant. After numerous trials it was found that a mixture, consisting of 70 parts melted rubber and 30 parts unbleached beeswax, softened with a little vaseline, served the purpose quite well, protecting the stopcocks completely. More than 150 determinations have been made in the same eudiometer without accident to stopcocks.

Some difficulty was experienced in expelling air from the copper oxide when the apparatus was being prepared for work. In beginning a series of determinations several days were often required for the purpose. The porcelain tube was strongly heated, while a slow stream of carbon dioxide was maintained, and the copper oxide was not considered to be in proper condition for use until the escaping carbon dioxide was found to be absorbed without residue by potassium hydroxide solution. About 300 c.c. of the escaping gas were used for the trial. When the copper oxide was freed from air, determinations of nitrogen in natural gas could follow each other until from experience it was shown to be necessary to reoxidize the partially reduced copper oxide. About ten determinations could be made before this reoxidation was needed. Regeneration of the copper oxide was effected by drawing air through the apparatus while hot. It was found that the copper oxide when once impregnated with carbon dioxide *while strongly heated* could be reoxidized by an air current with very little tendency to occlusion of air. After the passage of air for a few hours, a stream of carbon dioxide readily expelled the remaining air and the apparatus was again ready for further determinations. But if the copper oxide was allowed to cool in contact with air, much time was lost in removing the air by the current of carbon dioxide, even when strong heat was applied during the process. It appears that little or no occlusion of air takes place when the copper oxide is first impregnated with carbon dioxide, while the same substance exposed to air in the cold occludes the air and holds it with much persistence.

SELECTION OF SAMPLES OF GAS.

Many of the wells are drilled through several different gas producing sand rocks, separated by deep layers of impervious shales and other strata. The gas from these different sands mingles, and the product flowing from a single well is often a mixture of gas from formations many hundred feet apart in the vertical scale. It was attempted as far as possible in the present work to secure samples from wells yielding gas from a single sand rock. It was desirable that the samples be taken as far as possible from wells situated at no great distance from the laboratory, in order that as short a time as possible should elapse between the collection of the sample and the commencement of the analysis.

RESULTS OF DETERMINATIONS OF NITROGEN.

1. Gas well at Shields, 14 miles west of Pittsburgh. This well was drilled in 1892, and yields gas exclusively from the Fourth Sand, which was reached in drilling at a depth of 1,760 feet.

Date of Collection of Samples.	Percentage of Nitrogen found.	
August 5, 1896	(1)	1.25
	(2)	1.26
February 5, 1897	(1)	2.70
	(2)	2.67
	(3)	2.68
April 6, 1897	(1)	1.79
	(2)	1.80
April 20, 1897	(1)	1.85
	(2)	1.85
June 1, 1898	(1)	1.10
	(2)	1.10

2. Well on the Anderson farm at Sewickley, 12½ miles west from Pittsburgh. This well was drilled in 1894, and yields gas exclusively from the Third Sand, which was found at a depth of 1,850 feet.

Date of Collection of Samples.	Percentage of Nitrogen found.
July 7, 1896	(1) 2.48
	(2) 2.50
August 14, 1896	(1) 1.72
	(2) 1.71
March 22, 1897	(1) 2.11
	(2) 2.10

3. Well on the Müller farm at Glenfield, Pa., 9½ miles west from Pittsburgh. Drilled in 1887. The gas is produced mainly from the Fourth Sand, although a little gas finds access to this well from the upper sands. The Fourth Sand was reached in this well at a depth of 1,800 feet.

Date of Collection of Samples.	Percentage of Nitrogen found.
July 27, 1896	(1) 1.52
August 17, 1896	(1) 1.69
	(2) 1.69
April 2, 1897	(1) 3.24
	(2) 3.25
April 16, 1897	(1) 3.23
	(2) 3.21
April 28, 1897	(1) 3.23
	(2) 3.20
May 4, 1897	(1) 3.20
	(2) 3.22
April 8, 1898	(1) 2.10
	(2) 2.10
April 21, 1898	(1) 2.12
	(2) Lost.
June 9, 1898	(1) 1.27
	(2) 1.30
June 13, 1898	(1) 1.23
	(2) 1.22

4. Well on the Bayley farm, Neville Island in the Ohio River, 6½ miles west from Pittsburgh. The well was drilled in 1892. Gas is

derived from the "thirty-foot" sand alone, which rock was found at a depth of 1,510 feet.

Date of Collection of Samples.	Percentage of Nitrogen found.	
August 1, 1896	(1)	1.46
	(2)	1.48
April 12, 1897	(1)	2.10
	(2)	2.11
April 24, 1897	(1)	2.10
	(2)	2.09
May 27, 1898	(1)	1.49
	(2)	1.48

5. Well on the Hamilton farm, Neville Island in the Ohio River, 7 miles west from Pittsburgh. The gas was derived from the Third Sand, which was reached at a depth of 1,580 feet, although there was a slight flow of gas from the Fifth Sand, which was reached at 1,729 feet. The well was drilled during the spring of 1898. The first sample of gas below mentioned was taken about 24 hours after the gas had been turned into the mains.

Date of Collection of Samples.	Percentage of Nitrogen found.	
May 16, 1898	(1)	1.78
	(2)	1.76
May 19, 1898	(1)	1.74
	(2)	1.74

6. Well on the King farm at Murraysville, 18 miles east from Pittsburgh. The gas is derived from the Murraysville Sand at a depth of 1,336 feet. The well was drilled in 1887. Analyses of samples taken on a single date are presented, but this gas is of interest in the present connection, as the Murraysville gas field was among the earliest explored. The pressure in the rock has fallen from about 500 pounds to so low a point that at certain seasons of the year, when the demand is greatest, the gas is regularly pumped from the wells into the mains. Pumping was not in progress when the samples were taken.

Determinations of nitrogen in samples collected June 6, 1898, gave: —

(1) 1.29.
(2) 1.28.

7. Another well on the same farm at Murraysville yields gas exclusively from a sand about 100 feet deeper. Gas collected on the same

date from this well was found to contain the following percentages of nitrogen: —

(1) 1.38.
(2) 1.40.

8. Well on the Souder farm, 12 miles east of Buffalo. This well was drilled in 1892, and yields gas from the Trenton Limestone exclusively. Mr. E. Coste, Engineer for the Provincial Natural Gas Company of Buffalo, is authority for the statement that the drill passed through the base of the Trenton Limestone 30 feet below the point at which the gas was obtained. Hence the horizon from which this gas comes is extremely low in the geological scale as compared with the productive formations of the Pennsylvania gas fields.

Samples were collected at this well on September 3, 1896. The results of the analyses are as follows: —

(1) 4.57.
(2) 4.55.

9. Well on the Reinhart farm, near Sherkston, 10 miles east from Buffalo. In this well the gas is derived solely from the Clinton Limestone, which was reached at a depth of 590 feet. Examinations were made of samples collected on September 1, 1896. Percentage of nitrogen found: —

(1) 3.64.
(2) 3.61.

10. Well No. 12 of the Provincial Natural Gas Company at Sherkston, Canada. Gas is derived solely from the Medina Sandstone, which was reached at a depth of 850 feet.

The samples were collected on September 1, 1896. Percentage of nitrogen found: —

(1) 5.17.
(2) 5.10.

In the case of all these Canadian wells the gas samples were shipped at once to the laboratory, and the determinations made without delay. All the samples so far mentioned were taken directly at the wells. Several determinations of nitrogen have been made in the case of natural gas from the mains supplying Allegheny. This gas was derived from various wells scattered through a region of considerable area.

Date of Collection of Samples.		Percentage of Nitrogen found.
August 25, 1896	(1)	1.48
	(2)	1.50
August 26, 1896	(1)	1.52
	(2)	1.52
August 28, 1896	(1)	1.56
	(2)	1.54
August 28, 1896	(1)	1.52
	(2)	1.52
February 28, 1898	(1)	1.93
	(2)	1.99
March 9, 1898	(1)	1.30
	(2)	1.31

Careful tests for oxygen were made in the case of the gas from the mains, as there was a possibility of access of air to the gas. The method of testing consisted in causing the gas to bubble through a solution of manganous sulphate, to which a little sodium hydroxide had been added. A change in color of the manganous hydroxide which was precipitated would have indicated oxygen. Tests made in this way were continued frequently for an entire day while the nitrogen determinations were in progress, but no oxygen was found, and hence no air could have gained access to the gas.

There seems to be reason for the assertion that fluctuations occur in the composition of natural gas, but until the study of the subject is carried further, and more complete data obtained, no attempt can be made to connect such fluctuations with any known facts as to the geology of gas.

There is some little evidence for supposing that gas from the deeper horizons is richer in nitrogen, and that the older productive wells yield gas containing a little less nitrogen, but such may prove not to be the case when more data are at hand.

It seemed to be of interest to subject the incombustible gas residue, obtained in the preceding work, to further study. Portions of this residue were mixed with oxygen and subjected to the action of electric sparks. The experiments are still in hand, and their results will be presented in a later paper. It may be mentioned here that the gas subjected to this treatment yields oxides of nitrogen, and in presence of caustic alkali undergoes a considerable shrinkage in volume.

If natural gas occurs in liquefied form in the rocks owing to the pressure to which it is there subjected, it is probable that when a drill taps the gas-bearing rock, causing relief of pressure, the more volatile among the constituents of the liquefied gas would escape in relatively larger proportion at the outset. The process occurring would be of the nature of fractional distillation, and would tend to the production of a gas especially rich in the most volatile constituent; but the most volatile constituent of natural gas is nitrogen, since all of the hydrocarbons and carbon dioxide would be more readily liquefied than nitrogen. The first yield of a gas well should therefore contain a higher proportion, relatively, of nitrogen, and this nitrogen should gradually diminish as the liquefied gas continued to evaporate. There would result after a time a gaseous mixture containing less and less of nitrogen, and when the reduction of pressure had progressed so far as to permit of the conversion of the least volatile of the constituents into gas, the proportion of nitrogen in the escaping gas would become constant, because the process would then be one of outflow of a gas mixture, and not of volatilization of an extremely low boiling liquid whose constituents have different boiling points.

If natural gas occurs liquefied in the rocks, we should expect to find that the newly drilled wells yield at first a gas relatively richer in nitrogen. The rock pressure in the Pennsylvania natural gas fields has in rare instances attained to 1,000 pounds per square inch. Some cases are reported in Northern New York State where rock pressures of 1,500 and 2,000 pounds have been measured. Such pressures are probably the highest ever observed in any natural gas field, but such pressures would be insufficient to liquefy natural gas. Should further determinations of nitrogen furnish evidence that a gradual diminution of the percentage of nitrogen is in progress, support would be given to the view that natural gas occurs in liquefied form in the rocks. The great productiveness of many single wells is, upon this supposition, more readily explained, for in the interstices of the rock might be stored a much larger quantity of gas if in liquefied form. The study of the composition of natural gas will have much to do with determining this point.